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(54) Title of the Invention: Refrigerating machine oil.

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SPECIFICATION

1. TITLE OF THE INVENTION.

Refrigerating machine oil.

2. PATENT CLAIM.

A refrigerating machine oil comprising apolyvalent alcohol ester or mixture of a polyvalent alcohol ester and a mineral oil or a synthetic oil, to which mixture has been added 0.05-10 wt.% of a glycidyl ester of a straight chain unsaturated fatty acid with a carbon number of 14-18 or a straight or a side-chain (sic) saturated fatty acid with a carbon number of 8-18.

3. DETAILED DESCRIPTION OF THE INVENTION.

Sphere of Application in Industry.

This invention relates to a refrigerating machine oil, and more particularly to a refrigerating machine oil which in the presence of flons does not decompose the flons, does not corrode metal such as steel, copper, aluminium and the like, and moreover has itself excellent stability.

Technology of the Prior Art.

Recently, together with the increased standards in the refrigeration and freezing industry and in all kinds of industrial equipment, the use of flons has been tried in a wide range of fields like refrigeration or efficient waste energy use. Examples of these include primarily refrigerating and air conditioning equipment, and also the cooling of insulating oils in for example transformers, rectifiers and the like, and flon turbines. In machinery which uses these flons, there occur problems such as the degradation of the oil and corrosion of metal apparatus components, due to hydrogen chloride generated by flon decomposition or reactions between the oil and the flon.

Recently, synthetic oils such as naphthene type mineral oils, alkylbenzene type oils, polyether type oils and the like have been used for refrigerating machine oils, but the flon stability cannot be said to be satisfactory. Therefore, the addition of epoxidised vegetable oils, epoxidised fatty acid esters, and glycidyl ethers such as phenyl glycidyl ethers, as hydrogen chloride scavengers has been attempted (Tokko 57-42119, Tokko 60-19352, Tokkai 57-177097, Tokkai 59-102990, Tokkai 59-117590 and Tokkai 60-130696). Further, the addition of acrylic acid glycidyl esters and the like has been attempted (Tokkai 59-911198). However, several of these epoxy compounds strongly irritate the skin and their use is undesirable.

Recently, with the increasing efficiency of refrigerating machines and with attention being placed on the thermal stability of the refrigerating machine oils, polyvalent alcohol esters have come into use as refrigerating machine oils. Ester type oils are greatly superior to naphthene type mineral oils and alkyl benzene type oils as

regards their lubricating properties and stability at high temperatures. Moreover, ester type oils are used at higher temperatures than naphthene type mineral oils and alkylbenzene type oils, and therefore it can be said that they have superior stability at high temperatures, however their flon stability is not satisfactory, and it is difficult to control the corrosion of apparatus metal components. In order to overcome this point, the use of additives has been attempted (Tokkai 55-155093, tokkai 58-15592), but, not only is the solubility of the additives in the ester type oils not satisfactory, but also the thermal stability of the additives is inferior to that of the ester type oils, and satisfactory effects are not demonstrated under severe conditions. Namely, in the prior art, even if the conventionally used prior art epoxy compound additives are added, it is difficult to satisfactorily control the corrosion of metal components.

Problems to be Overcome by this Invention.

The performances demanded of refrigerating machine oils used in refrigerating machines which must be operated continuously for long periods under severe conditions, of course relate to the lubricating properties, and also high temperature stability and flon stability.

The object of this invention is to put forward, by the use of a novel additive with excellent compatibility with the base oil, a refrigerating machine oil with which even under severe conditions, flons are stabilised, and the corrosion of apparatus metal components can be suppressed.

Technique for Overcoming the Problems of this Invention.

These inventors as a result of assiduous investigations into additives which inhibit the corrosion of apparatus metal and also increase the flon stability in ester type refrigerating machine oils, discovered the effectiveness of glycidyl esters of fatty acids. This invention is founded on this knowledge.

Namely, this invention comprises a refrigerating machine oil characterised in that to a polyvalent alcohol ester or a mixture of a polyvalent alcohol ester, and a mineral oil or synthetic oil, is added 0.05-10 wt.% of a glycidyl ester of a straight chain unsaturated fatty acid with a carbon number of 14-18, or a straight chain or side-chain (sic) saturated fatty acid with a carbon number of 8-18.

As the polyvalent alcohol ester in this invention, there may be used for example esters of polyvalent alcohols and monocarboxylic acids (Tokkai 56-133421), and esters composed of polyvalent alcohols, and dicarboxylic acids and monocarboxylic acids (Tokkai 59-164393). In these esters, the polyvalent alcohol is preferably a neopentyl polyol such as dipentaerythritol, pentaerythritol, trimethylol propane, neopentyl glycol and the like.

Further, the synthetic oil or mineral which can used together with the polyvalent alcohol ester may be a synthetic oil such as a polyether type, an alkylbenzene type, a polyolefin type or the like, or a mineral oil such as a paraffin type, naphthene type or the like generally used as a lubricating oil.

The fatty acid which forms the fatty acid glycidyl ester used in this invention comprises a straight chain unsaturated fatty acid with a carbon number of 14-18, or, a straight chain or side chain (sic) saturated fatty acid with a carbon number of 8-18. Glycidyl esters of fatty acids having a carbon number below these ranges have unsatisfactory solubility with respect to the ester type base oils, and further, in some cases they irritate the skin and are therefore undesirable. Glycidyl esters of fatty acids having a carbon number above the said ranges, form a white suspension at low temperature when dissolved in ester type base oils, and are therefore undesirable. Examples of these fatty acids include caprylic acid, 2-ethylhexane (sic), nonanoic acid, isononanoic acid, 2,2-dimethylnonanoic acid, capric acid, 3-methyldecanoic acid, lauric acid, myristic acid, isostearic acid, tetradecenoic acid, palmitoleic acid, oleic acid, linoleic acid and the like.

In accordance with this invention, the quantity of fatty acid glycidyl ester added is 0.05-10 wt.%, preferably 0.2-4 wt.%, with respect to the ester type base oil. When less than 0.05 wt.% is added, the target effect cannot be obtained, and further if more than 10 wt.% is added, white clouds are generated at low temperatures and this is undesirable.

The fatty acid glycidyl esters of this invention can be used together with other additives such as antioxidants, antiwear agents and the like.

The refrigerating machine oil of this invention can be widely applied in all refrigerating machines using flons.

Action.

In this invention, the reason why the fatty acid glycidyl esters stabilise the systems in the presence of flons, is thought to be that the epoxy groups within the molecule scavenge hydrogen chloride formed by flon decomposition. The reason why the fatty acid glycidyl esters of polyvalent alcohols of this invention are particularly effective for polyvalent alcohol esters is not clear, but the chemical structures of these compounds are similar, and it is thought that the excellent compatibility is one cause.

Effects of this Invention.

Refrigerating machine oils composed of a polyvalent alcohol ester type oil and a fatty acid glycidyl ester in accordance with this invention, not only have excellent lubricating oil properties and thermal stability, but comprise refrigerating machine oils with improved flon stability. Therefore, by the use of the refrigerating machine oils of this invention, it will be possible to operate refrigerating machines under severe conditions over long periods without problem.

EXAMPLES

This invention will now be described in greater detail by reference to Examples.

The ester oils, mineral oils and alkylbenzene (sic) used in the Examples and

Comparative Examples are shown in Table 1.

The fatty acid glycidyl esters and other epoxy compounds used in the Examples and Comparative Examples are shown in Table 2.

The additives shown in Table 2 were added to the base oils of Table 1 and their mixtures, and refrigerating machine oils produced. The obtained refrigerating machine oils were evaluated by a Sealed Tube Test.

The Sealed Tube Test:-

Into a glass tube (internal diameter 6 mm, thickness 2 mm) were introduced 0.6 ml refrigerating machine oil, copper rods (ø2x50 mm), steel rods (ø2x50mm) and aluminium foil (2x30 mm). Flon-22 (chlorodifluoromethane) was then introduced in a cooling bath (?) at -60°C, and the tube sealed. A heating test was carried out for 5 days at 200°C, and changes in the hue of the samples, the quantity of hydrogen chloride present, the presence or absence of copper plating phenomenon, the state of corrosion of the steel rods and the state of corrosion of the copper rods determined.

Further, the properties of each refrigerating machine oil were observed at -20°C.

The test compositions and the results obtained are shown in Table 3. The symbols for each test in Table 3 have the following meanings.

The change in hue shows the differences in hue between before and after the heating test, wherein the smaller the number the better (a 10 stage evaluation of 1 (pale colour, best) to 10 (dark colour, worst)).

The smaller the quantity of hydrogen chloride present the better.

O: Less than 25 ppm.
Δ: 25-100 ppm.
X: More than 100 ppm.

The copper plating phenomenon shows the degree of plating of the steel rod, and none is preferably observed.

O: None observed.
O: Very slight trace.
Δ: Slight.
X: A lot.

The less corrosion of the copper and steel rods the better.

O: Almost none observed.
Δ: Slight corrosion.
X: Severe corrosion.

As far as the properties of the refrigerating machine oils at -20°C are concerned, a transparent liquid is preferable.

O: Transparent liquid.

X: White cloudy liquid.

TABLE 1

Key	Type	Polyvalent alcohol	Fatty acid	(wt.%)	Cloud pt. (°C)
a	ester	neopentyl glycol	caprylic acid	51	-25
			2-ethylhexanoic	49	or less
b	ester	trimethylol propane	caprylic acid	65	
			capric acid	30	-35
			lauric acid	5	or less
c	ester	pentaerythritol	2-ethylhexanoic acid	65	-35
			lauric acid	35	or less
d	ester	trimethylol propane	oleic acid	84	-25
			adipic acid	16	or less
e	ester	trimethylol propane	caprylic acid	82	-35
			adipic acid	18	or less
f	mineral oil	commercial naphthene type			
g	synthetic oil	commercial alkylbenzene type			

TABLE 2

Key	Epoxy Compound	Oxirane Oxygen (%)
A	2-ethylhexanoic acid glycidyl ester	7.0
B	nonanoic acid glycidyl ester	6.4
C	coconut oil fatty acid[1] glycidyl ester	5.1
D	synthetic fatty acid[2] glycidyl ester	6.5
E	oleic acid[3] glycidyl ester	4.8
F	caproic acid glycidyl ester	7.8
G	behenic acid [4] glycidyl ester	3.6
H	erucic acid[5] glycidyl ester	3.6
I	epoxidised soy bean oil	6.9
J	long chain alcohol[6] glycidyl ester	5.5

Notes:-

1) C_8-C_{18} straight chain saturated fatty acid 92%
   C_{18} straight chain unsaturated fatty acid 8%
2) C_{7-9} side chain saturated fatty acid
3) C_{14-18} straight chain saturated fatty acid 15%
   C_{14-18} straight chain unsaturated fatty acid 85%

4) C_{22} straight chain saturated fatty acid 65%

5) C_{22} straight chain unsaturated fatty acid 90%

6) C_{12} alcohol 55%
   C_{14} alcohol 45%

TABLE 3

	Test	Refrigerating Machine Oil			Change	HCl	Cu	Cu	Steel	Properties
		Base Oil	Additive	wt.%	in hue	present	plating	corrosion	corrosion	(-20°C)
Invention	1	a	A	0.7	1	O	O	O	Δ	O
	2	b	A	0.07	1	Δ	O	O	O	O
	3	b	A	0.7	0	O	O	O	O	O
	4	b	A	7.0	0	O	O	O	O	O
	5	c	A	0.7	0	O	O	O	O	O
	6	d	A	0.7	0	O	O	O	O	O
	7	e	A	0.7	0	O	O	O	O	O
	8	b	B	0.7	0	O	O	O	O	O
	9	b	C	0.7	0	O	O	O	O	O
	10	b	D	0.7	0	O	O	O	O	O
	11	b	E	0.7	0	O	O	O	O	O
	12	b+f (1:1)	B	0.7	2	O	O	O	O	O
	13	b+g (1:1)	B	0.7	2	O	O	O	O	O
	14	e+f (1:1)	E	0.7	2	O	O	O	O	O
	15	e+g (1:1)	E	0.7	2	O	O	O	O	O
Comparison	16	a	-		4	X	X	Δ	X	O
	17	b	-		3	X	Δ	Δ	Δ	O
	18	c	-		2	Δ	Δ	O	O	O
	19	d	-		2	Δ	Δ	O	O	O
	20	e	-		2	Δ	Δ	O	O	O
	21	b	A	0.02	3	X	Δ	Δ	Δ	O
	22	b	A	12.0	1	O	O	O	Δ	X
	23	b	F	0.7	3	O	Δ	Δ	X	O
	24	b	G	0.7	0	O	O	O	Δ	X
	25	b	H	0.7	0	O	O	O	Δ	X
	26	b	I	0.7	3	O	Δ	Δ	X	X
	27	b	J	0.7	2	O	Δ	Δ	X	O
	28	b+f (1:1)	-		4	X	X	X	X	O
	29	b+g (1:1)	-		4	X	X	X	X	O
	30	e+f (1:1)	-		4	X	X	X	X	O
	31	e+g (1:1)	-		4	X	X	X	X	O

As is clear from the results shown in Table 3, compared to the comparative refrigerating machine oils, the refrigerating machine oils of this invention excel under all the headings of change in hue, quantity of hydrogen chloride present, copper plating phenomenon, copper corrosion, steel corrosion and low temperature properties, and it is evident that the refrigerating machine oils of this invention have most excellent flon stability.